Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

The Solvent effect and identification of a weakly emissive state in nonradiative dynamics of guanine nucleoside and nucleotide- A combined femtosecond broadband time-resolved fluorescence and transient absorption study

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Supporting Information

Description of Kerr-gate technique for recording femtosecond broadband time-resolved fluorescence and fluorescence anisotropy spectra:

A Kerr device comprising a ~1 mm thickness of quartz plate (Kerr medium) equipped with a crossed polarizer pair was used to function as an ultrafast shutter to sample broadband transient fluorescence signal at a series of designated pump-probe delay times. Part of the 800 nm fs laser (from Ti:Sapphire regenerative amplifier laser system) was applied as gating pulse (or also called probe pulse) to drive the Kerr device for attaining the fs wavelength-resolved fluorescence spectra.[1]

In the fs-TRF measurement, to obtain the overall fs-TRF spectra, in order to eliminate the effect due to rotational diffusion, the polarization direction of the pump laser was set at the magic angle relative to that of the first polarizer in the Kerr device.

For the measurement of fs-TRFA spectra (r(t)), the experiments were done by setting the polarization direction of the pump laser to be either parallel or perpendicular to that of the first Kerr-gate polarizer so as to measure the spectrum of $I_{para}(t)$ and $I_{perp}(t)$, respectively. The r(t) was then derived according to $r(t) = [I_{para}(t)-I_{perp}(t)]/[(I_{para}(t)+2I_{perp}(t)]$.[2,3]

Figure S1 Steady-state absorption (a, c and e) and steady-state fluorescence (b, d, f) spectra recorded with excitation at 267 nm (solid) and 285 nm (dotted) for dGMP in buffered (pH7) water (a, b), dG in buffered (pH7) water (c, d) and methanol (e, f) with different concentrations of 0.1 mM (red), 1 mM (green) and 10 mM (cyan)

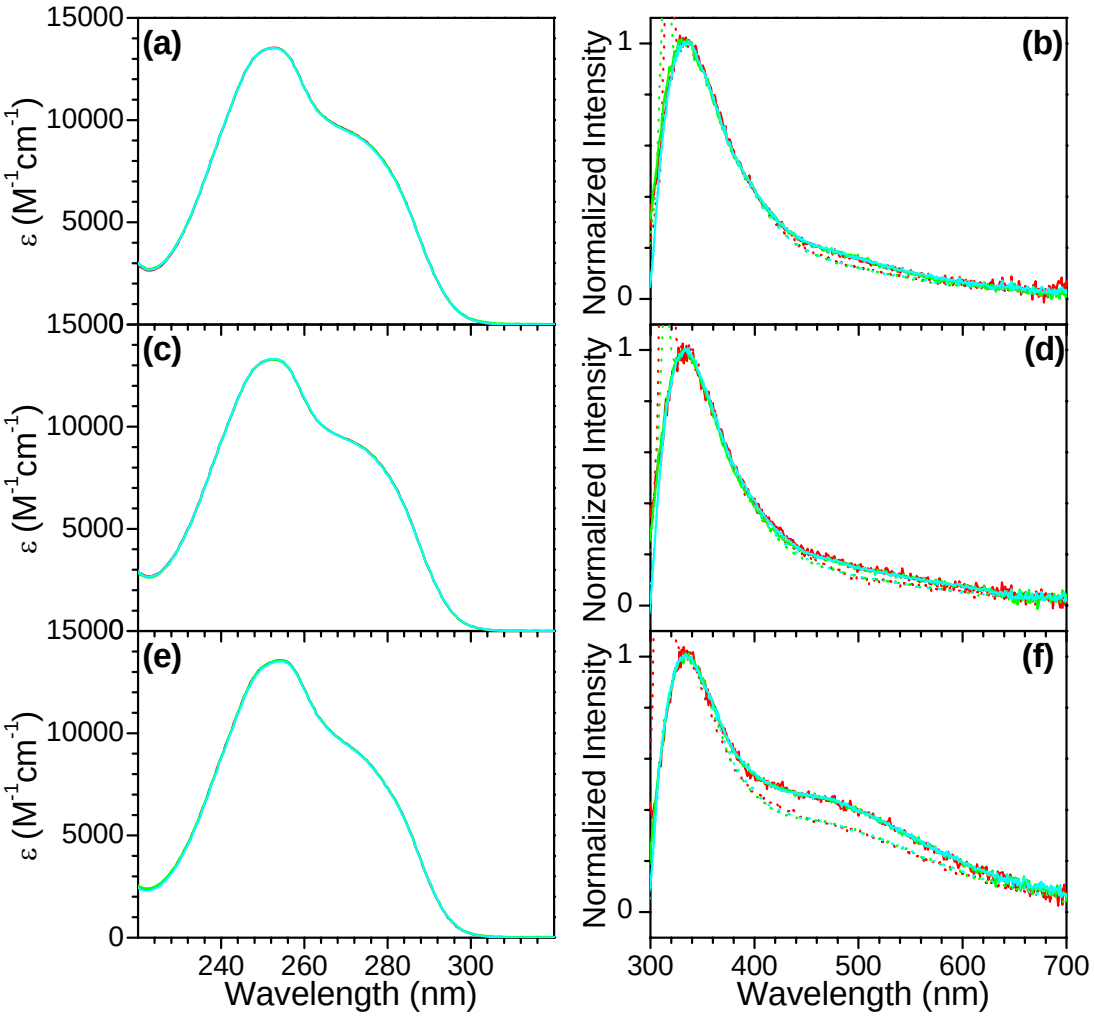

Figure S2 Upper panel: femtosecond time-resolved fluorescence spectra of dG (~2-5 mM) in buffered (pH7) water recorded at various delay times (0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.6, 0.7, 0.85, 1, 1.2, 1.4, 1.6, 1.8, 2, 2.25, 2.5, 2.75, 3, 3.25, 3.5, 3.75, 4, 4.5, 5, 5.5, 6, 6.5, 7, 7.5, 8, 8.5, 9, 9.5, 10 ps) after excitation at 267 (upper, left) and 285 nm (upper, right). Representative transient fluorescence spectra at indicated decay times are normalized with respect to their maximum intensities in order to show clearly temporal variation of the transient spectral profiles. Lower panel: experimental (circle, square, triangle) and fitted (solid lines) fluorescence decay profiles obtained for dG in pH7 buffered water with excitation at 267 (bottom, left) and 285 (bottom, right) nm.

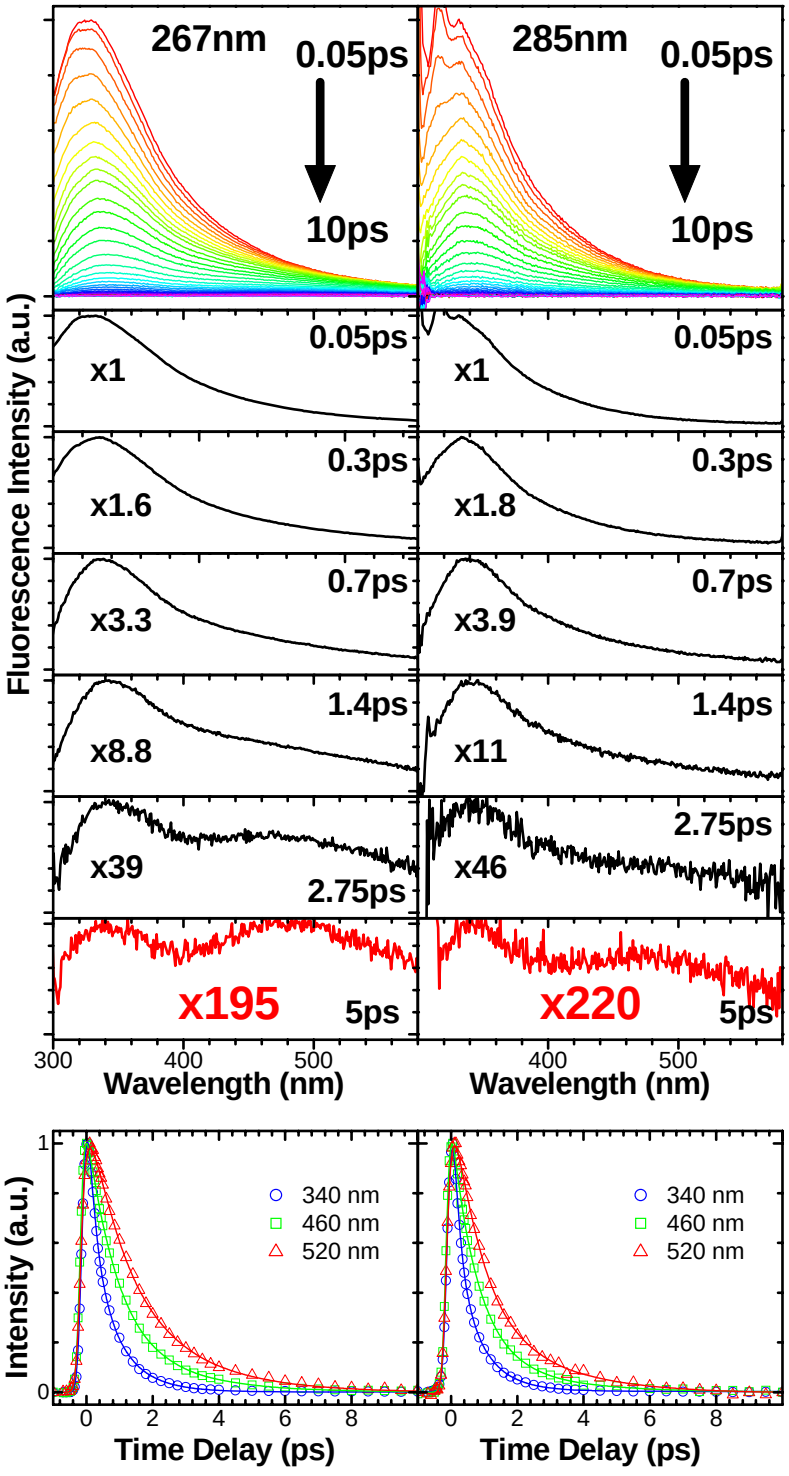

Table S1 Fitting parameters obtained from global analysis of the fs time-resolved fluorescence decay profiles at the representative wavelengths

dGMP in H_2O (pH7)							
λ_{ex} (nm)	λ (nm)	τ_1 (ps)	a_1	τ_2 (ps)	a_2	τ_3 (ps)	a_3
245	340		0.65		0.34		0.01
	460		0.01		0.73		0.26
	520		-0.24		0.32		0.43
267	340		0.57		0.42		0.00
	460	0.20 ± 0.03	-0.07	0.79 ± 0.04	0.68	1.98 ± 0.10	0.25
	520		-0.28		0.31		0.41
285	340		0.65		0.35		0.00
	460		-0.05		0.82		0.14
	520		-0.25		0.45		0.30

dG in H_2O (pH7)							
λ_{ex} (nm)	λ (nm)	τ_1 (ps)	a_1	τ_2 (ps)	a_2	τ_3 (ps)	a_3
267	340		0.52		0.47		0.01
	460		-0.14		0.63		0.23
	520		-0.29		0.32		0.39
		0.22 ± 0.02		0.77 ± 0.02		1.99 ± 0.11	
285	340		0.61		0.39		0.01
	460		-0.01		0.83		0.16
	520		-0.28		0.50		0.22

dG in CH_3OH							
λ_{ex} (nm)	λ (nm)	τ_1 (ps)	a_1	τ_2 (ps)	a_2	τ_3 (ps)	a_3
267	340		0.75		0.24		0.01
	460		-0.08		0.49		0.42
	520		-0.28		0.21		0.51
		0.24±0.02		1.01±0.04		4.10±0.16	
285	340		0.75		0.24		0.01
	460		-0.05		0.52		0.43
	520		-0.37		0.20		0.43

Note: the negative amplitudes of the τ_1 (ps) component observed with the decay traces at ~460 and 520 nm are due to the initial growth of TRF intensity at the respective wavelengths.

Figure S3 Comparison of the normalized fs time-resolved fluorescence spectra recorded at 5 ps after 285 (red), 267 (blue) and 245 nm (cyan) excitation of dG and dGMP in pH7 buffered water.

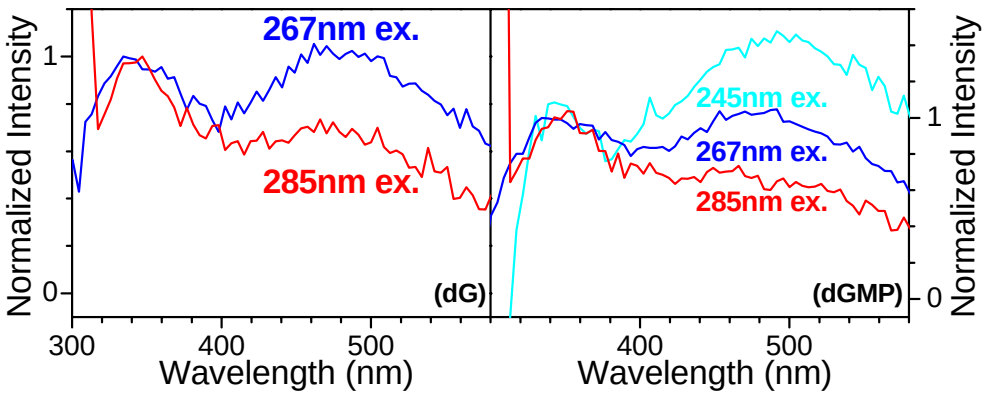

Figure S4 Fs time-resolved fluorescence anisotropy spectra of dG in pH7 buffered water (a, b) and methanol (c, d) at initial (~0 ps) and ~5 ps after excitation at 267 nm (a, c) and 285 nm (b, d).

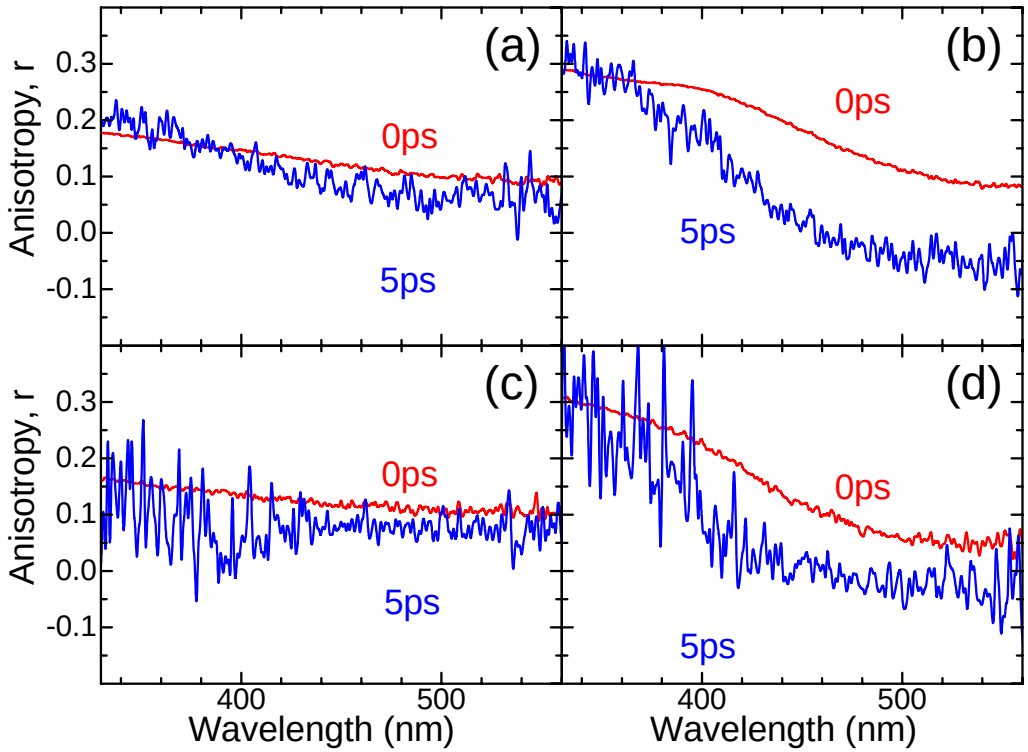

Figure S5 Temporal evolution of fs transient absorption spectra (220-400 nm) recorded after 267 nm excitation of dG in (a) pH7 buffered water (0.15, 0.2, 0.7, 1, 1.25, 1.5, 1.75, 2.5, 3, 3.5, 5, 7, 15 and 20 ps), (b) pure water (0.15, 0.2 , 0.7, 1, 1.25, 1.5, 1.75, 2, 2.5, 3, 3.5, 5, 7 and 20 ps) and (c) deuterated water (0.15, 0.2, 0.7, 1, 1.25, 1.75, 2, 2.5, 3, 4, 5, 6, 7 and 20 ps). # artifact from excitation laser.

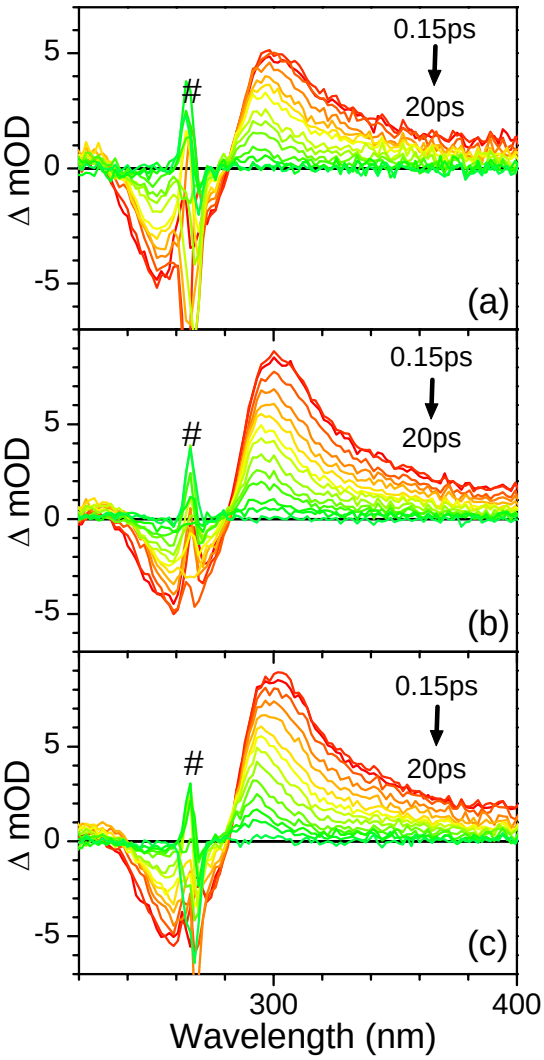

Figure S6 Experimental (square and circle) and fitted (lines) transient absorption decay profiles recorded at ~253 (square, inversion of the negative values) and 305 nm (circle) after the 267 nm excitation of dG and dGMP in pH7 buffered water (pH7), pure water (H_2O), deuterated water (D_2O) and methanol (CH_3OH).

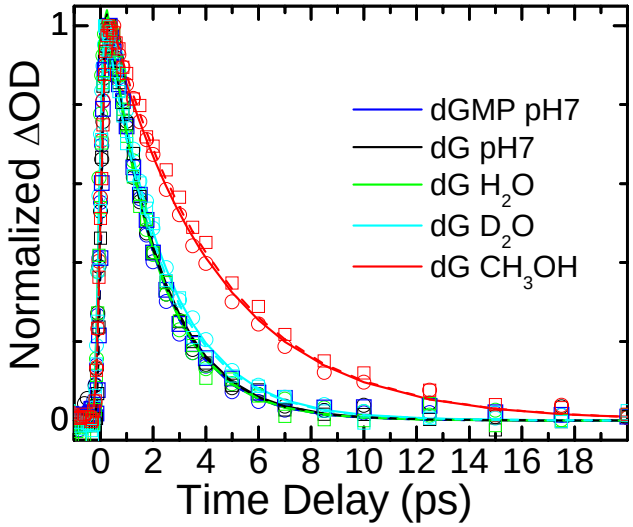

Table S2 Fitting parameters obtained from global analysis of the fs transient absorption decay profiles at the selected [a]probe wavelengths.

			dGMP (λ_{ex}=267 nm)				
	[a]λ_p (nm)	τ_1 (ps)	A_1	τ_2 (ps)	A_2	τ_3 (ps)	A_3
H_2O(pH7)	253					2.00	-1.00
	305						1.00
	350	0.27	-0.09	0.81	0.39		0.53
	520	0.27	0.45	0.81	0.55		
			dG (λ_{ex}=267 nm)				
	[a]λ_p (nm)	τ_1 (ps)	A_1	τ_2 (ps)	A_2	τ_3 (ps)	A_3
H_2O(pH7)	253					1.99	-1.00
	305						1.00
	350	0.23	-0.25	0.85	0.24		0.51
H_2O(neat)	253					1.94	-1.00
	305						1.00
	350	0.26	-0.27	0.85	0.34		0.40
D_2O	253					2.25	-1.00
	305						1.00
	350	0.25	-0.27	0.86	0.20		0.53
CH_3OH	253					4.10	-1.00
	305						1.00
	350	0.27	-0.17	0.79	0.24		0.59
	520	0.27	0.68	0.79	0.32		

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1. (a) W. M. Kwok, C. Ma and D. L. Phillips, Femtosecond time- and wavelength-resolved fluorescence and absorption spectroscopic study of the excited states of adenosine and an adenine oligomers, *J. Am. Chem. Soc.*, 2006, **128**, 11894 -11905; (b) W. M. Kwok, C. Ma and D. L. Phillips, A doorway state leads to photo-stability or triplet photo-damage in thymine DNA, *J. Am. Chem. Soc.* 2008, **130**, 5131 -5139; (c) W. M. Kwok, C. Ma and D. L. Phillips, "Bright" and "Dark" excited states of an alternating AT oligomer characterized by femtosecond broadband spectroscopy, *J. Phys. Chem. B*, 2009, **113**, 11527-11534; (d) C. T. L. Chan, C. C. W. Cheng, K. Y. F. Ho and W. M. Kwok, Femtosecond broadband time-resolved fluorescence and transient absorption study of the intramolecular charge transfer state of methyl 4-dimethylaminobenzoate, *Phys. Chem. Chem. Phys.*, 2011, **13**, 16306-16313.

2. F. A. Miannay, T. Gustavsson, A. Banyasz and D. Markovitsi, Excited-state dynamics of dGMP measured by steady-state and femtosecond fluorescence spectroscopy, J. Phys. Chem. A, 2010, 114, 3256-3263.

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